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ATOMIC FORCE MICROSCOPY BASED EDDY CURRENT IMAGING AND CHARACTERIZATION OF COMPOSITE AND NANOCOMPOSITE MATERIALS (PREPRINT)

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Carbon Fiber Composites, Nondestructive Evaluation, Interface Analysis

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ABSTRACT

Atomic Force Microscope (AFM) based eddy current imaging technique has been used to characterize carbon fiber reinforced composites and carbon nanofibers nanocomposite. The surface topography and eddy current images of the same region of the sample acquired at the same time are presented. While the contrast in AFM images is due to surface topography variations the contrast in the eddy current images is due to the local variation in the electrical conductivity of the sample. The results show that the combined techniques of AFM and eddy current imaging can be used effectively to investigate the distribution, dispersion of the carbon fibers in the polymer matrix and the fiber matrix interphase. An enhanced contrast at the interface between the fiber and the matrix has been observed in the eddy current images. The implications of the improved contrast in eddy current images and its application to investigation of fiber-matrix interface/interphase in carbon fiber polymer matrix composites is discussed.

KEY WORDS: Carbon Fiber Composites, Nondestructive Evaluation, Interface Analysis

1. INTRODUCTION

Ever since the development of carbon nanotubes by Ijima (1), researchers have been investigating carbon nanotubes for use in high strength applications, due to their remarkable physical properties (2-4). Carbon nanotubes exhibit high strength and a relatively low density. During the last decade, there have been several research works to study CNT reinforced polymer matrix composite systems. One potential application for these nanocomposites is in aircraft systems which can provide high strength but with lower weights. Even though the carbon nanotubes hold much promise for many applications, there are several unresolved issues. The major problems are related to the dispersion of the CNTs in the matrix and the adhesion between the nanotubes and the matrix. Several attempts have been reported in literature to overcome these

problems (5,6). One such attempt is to functionalization of nanotubes. But it proved to be difficult due to limited access to separate sites on nanotubes. Therefore, as an alternative, carbon nanofiber (CNF) is increasingly used as a low-cost version of CNT. Although the mechanical properties of CNF are not as good as those of CNT, the modulus of elasticity and the strength of CNT's are still relatively high (5). Therefore, CNF reinforced composites are increasingly gaining the attention of researchers (5, 7, 8, 9).

A literature search in the field of CNF reinforced composites shows that majority of research efforts mainly focuses on the manufacturing and processing related issues of the composites. The characterization of nanocomposites is done by traditional techniques such as tensile and bending tests (5, 7, 8, 9). However, these characterization techniques are macroscopic in nature. Further more, the homogeneous dispersion and adhesion of the fibers to the matrix is a major concern in CNF reinforced composites. Therefore, this study focuses on the use of an Atomic Force Microscopy (AFM) based eddy current imaging technique to characterize the carbon nanofibers in the composites with nanometer resolution. AFM is routinely used to characterize the surface of both conductors and insulators with a nanometer resolution (10, 11). Several modifications to the AFM to image material properties on nanoscale have been reported in literature (12-15).

Eddy current testing is one of the most frequently used nondestructive evaluation NDE method to detect defects in conducting materials (16, 17, 18). The basic principles of eddy current measurements involve exciting a coil with an electromagnetic signal placed near a metallic specimen. The oscillating magnetic field generated by the coil induces eddy current in the metal. The eddy currents in the metal produce an opposing magnetic filed to that of the exciting coil. The effect is measured by the change in the electrical impedance of the coil. The strength of the eddy current depends on the electrical conductivity of the metal. Thus presence of defects in the metal modify the eddy current generation in the metal thereby changing the impedance of the coil. This simple methodology has not only been used for NDE applications but also in the measurement and characterization of electrical properties of materials under different environmental conditions. The resolution in eddy current imaging systems is limited by the diameter of the coil. The best eddy current microscope that has been developed in any laboratory has a resolution of about 500 μm. This microscope uses specially developed tiny coils for imaging applications.

In the last decade there here have been attempts to obtain eddy current images based on AFM (19, 20). The basic principle of the methodology has been to observe the change in the amplitude of vibration of a magnetic tip- cantilever system when brought close to a metallic material. A vibrating magnetic tip near a metal produces eddy current in the metal. An opposing magnetic field generated by the eddy currents in the metal reduces the amplitude of the vibrating magnetic tip. The change in the vibration characteristics of the cantilever is used to produce eddy current images. In the AFM based eddy current imaging, stiff cantilevers with magnetic tip are used and the AFM is operated in the intermittent contact mode. In this study, we have developed an eddy current imaging system based on AFM operating in the so-called Lift mode of AFM while utilizing a flexible cantilever with a magnetic tip. In our method, a tiny coil placed under the sample, excited with an AC signal generates eddy current in the material. A flexible magnetic tip-cantilever is brought close to the opposite face of the sample. Under the influence of the oscillating magnetic filed of the coil, the magnetic tip-cantilever will vibrate. The presence of a

conducting sample between the coil and the magnetic tip-cantilever will change the vibration characteristics. The changes are measured with an external electronic instrumentation and used to obtain eddy current images with very high resolution. This technique was used to characterize a carbon fiber reinforced composite and a nanocomposite sample. The difference in the conductivity between the carbon fibers and the polymer matrix is exploited to investigate both traditional carbon fiber composites as well as nano-carbon fiber composites. The results show that the technique can be successfully used to characterize the nanocomposites with nanometer resolution.

2. MATERIALS AND EXPERIMENTAL METHOD

Two composite samples were studied using the eddy current imaging technique. The first sample that was characterized has 7µm diameter carbon fibers reinforced in Polyetheretherketone (PEEK) matrix. The second sample was a nanocomposite thin film with vapor grown carbon nanofibers (VGCF) inside a polymer matrix. Nanocomoposite films were fabricated with Vapor Phase Grown Carbon Nanofibers (Pyrograf III PR-24-LHT, Applied Science, Cedarville Ohio). Most of the nanofibers are agglomerated in bundles of 20-200 micrometers in diameter (Figure 1A). The individual nanofibers are about 100 nanometers in diameter (Figure 1B) and highly graphitic. It is a processing challenge to de-agglomerate the raw material and uniformly disperse into a polymer resin. In this study, we dispersed the nanofibers into a solution of high performance thermoplastic polymer in DMAC at a loading of 5 wt% (relative to the polymer). The solution was exposed to high shear conditions using laboratory and pilot plant equipment for about 1 hour. The resulting solution was cast onto a glass plate using a doctor blade, and heat was applied to evaporate the solvent. The resulting free standing films were then analyzed with microscopy. While most of the nanofibers were well dispersed, some agglomerates of approximately 10-20 micrometers still remained.

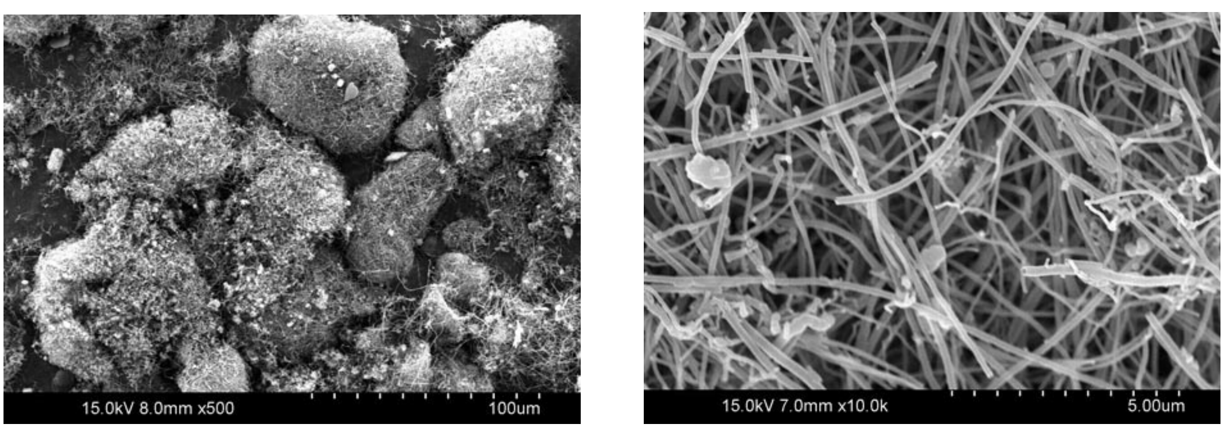

Figure 1 High resolution SEM images of raw Pyrogarf III carbon nanofibers, A) 500X magnification, showing agglomerated nature of raw materials, and B) 10kX maganfication showing individual nanofibers within an agglomerate.

A Digital Instruments Dimension 3100 AFM was used to obtain surface topography and eddy current images. AFM utilizes a sharp tip, 20-30 nm in radius, attached to a cantilever 100 µm long usually made of Si_3N_4 and raster scanned across the sample surface to obtain topographic information (10). A laser light is reflected on the back of the cantilever and the deflection of the cantilever is detected by a split photo diode detector. Imaging is accomplished by keeping the deflection of the cantilever constant by means of a feedback loop and vertically moving the piezoelectric scanner at each data point to maintain a set point deflection. The distance the scanner moves vertically at each data point is stored by the computer to form the topographic image of the surface. The resolution in the AFM depends on the diameter of the tip and resolution in this study is in between 30-60nm.

To perform the eddy current imaging, the basic AFM setup was modified using external instrumentation. Instead of a standard AFM tip, a magnetic coated Silicon Nitride tip with a nominal tip diameter of 40 nm and spring constant of 0.1N/m was used. The sample was placed on a coil and was excited by an AC power source in the range of 50 KHz-500 KHz. The magnetic fields generated by the coil oscillate the magnetic tip and the cantilever, and the eddy currents generated in the sample modify these vibration characteristics depending on the local electrical conductivity. The out put of the photo-detector which is the vibration characteristics of the cantilever, and the signal that excites the coil under the sample are fed into a lock-in amplifier. The out put of lock-in amplifier is used to generate eddy current images. The AFM was operated in the lift mode. In lift mode, the tip traces the topography of the sample surface in the first pass and then lifts to the user selected height (usually between 50-200nm) and then takes the second pass, where the magnetic tip responds to the magnetic field generated in the sample. The contrast in the eddy current images is related to the variation of the electrical conductivity of the sample. Whenever the local conductivity of the sample varies, there would be a change in the amplitude of the signal and that change in amplitude is related to the electrical conductivity variation of the sample. Fig.1 shows a general schematic diagram of the AFM/Eddy current imaging setup.

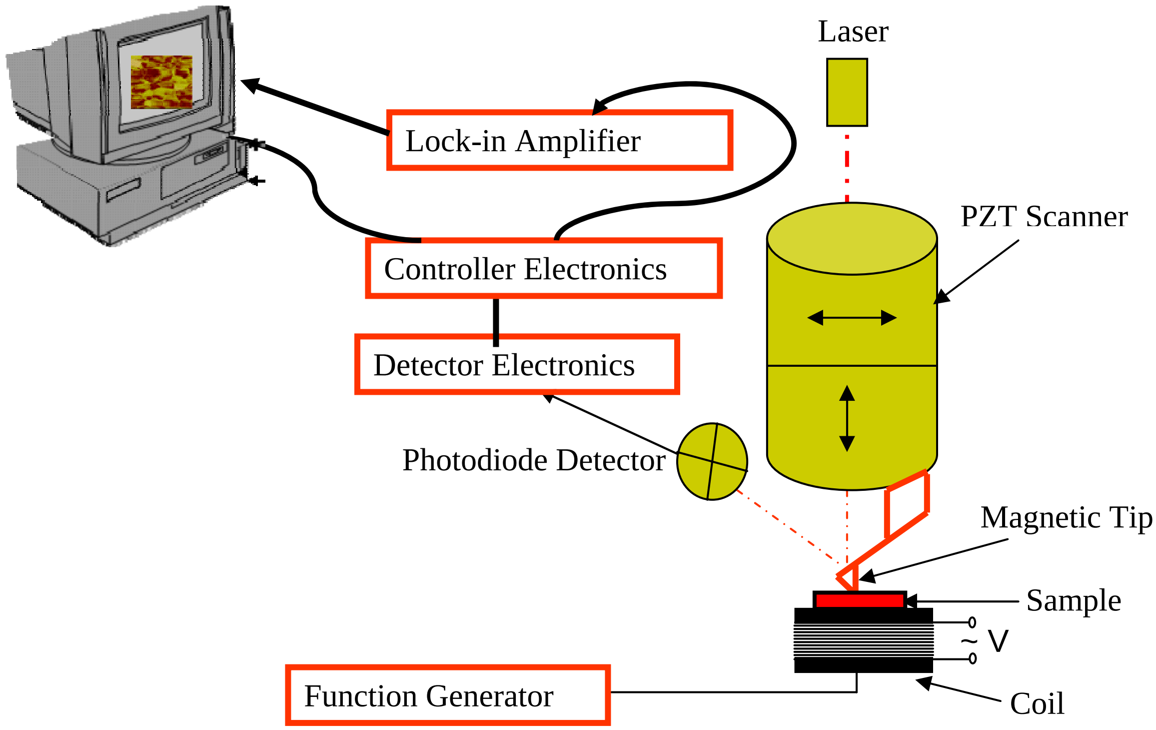

Figure 2 A general schematic of eddy current imaging setup using AFM.

3. RESULTS AND DISCUSSION

Eddy current imaging was first done on a carbon fiber reinforced polymer with approximately 7µm diameter fibers. In all the images that follow, the image on the left is that of topography and the right is an eddy current image. The AFM topography and eddy current images are simultaneously acquired at a selected region of the sample. Fig. 2 shows the topography and eddy current image on the composite sample.

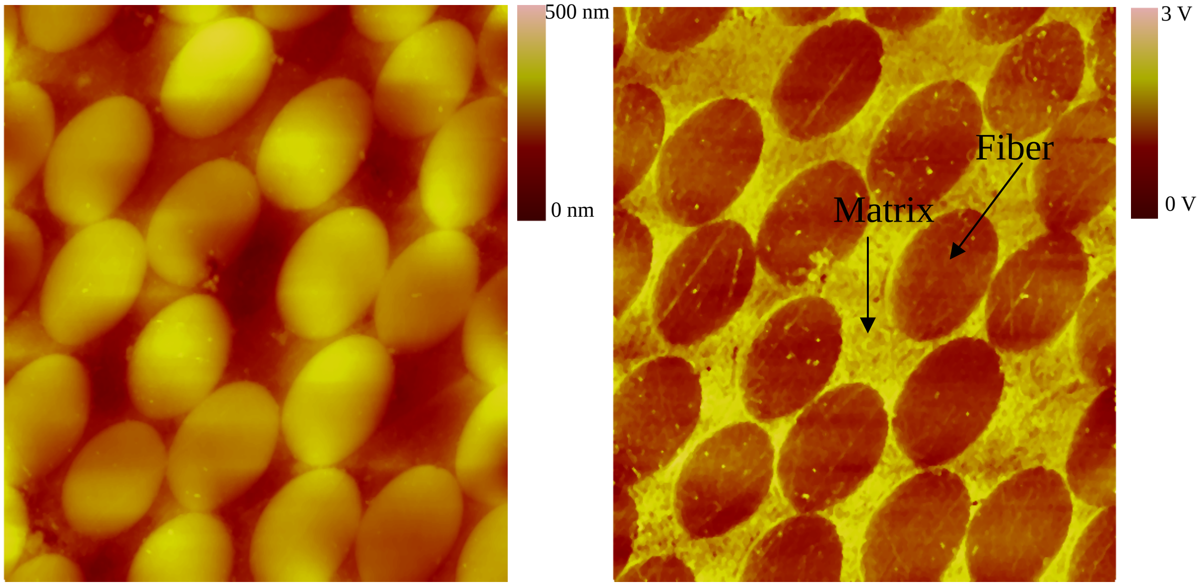

Figure 3 AFM topography (left) and eddy current image (right) of carbon fibers reinforced in a polymer matrix. Scan size 30 µm X 30 µm. Eddy current image shows conductive fibers and nonconductive matrix with distinct contrast difference.

The image on the left of Fig.2 shows the topography of carbon fibers in the polymer matrix. The contrast in the AFM image is due to variation of surface height and brighter regions indicate higher surface heights. The surface height of the features in this image is about 500 nm, with a scan size of 30 µm X30µm. The image on the right shows the eddy current image of the same region. The eddy current image clearly shows the fibers and the polymer matrix. This difference in the contrast between the fibers and the matrix is due to the variations in the conductivity of fiber and polymer. While carbon fibers are conductive, the polymer matrix is not. The generation of eddy currents dampens the oscillation of the magnetic cantilever above the sample surface (19). Hence when the tip scans over the sample, the conductive regions of the sample dampen the oscillations of the cantilever, but above the nonconductive regions of the sample, the cantilever vibrates without dampening. Consequently, in eddy current images, darker contrast indicates higher conductivity regions and brighter contrast indicates less conductivity regions. The arrows on the eddy current image show the conductive fibers and nonconductive matrix.

A section analysis of a region of the eddy current image in fig 2 is shown in figure 3. The section analysis shows the conductivity variations in fiber and matrix. Fig 3 shows the region where the section analysis is done. The image on the right shows the conductivity profiles of the region selected. It can be seen that the profile above the center line represents the matrix and the profile below the center line represents the fiber. This is due to the fact that the conductive fibers dampen the oscillation of the cantilever and hence is seen with lower amplitudes in the section analysis. Variations of the conductivity within a fiber can be seen in conductivity profile. It can also be seen from this analysis that, at some regions there is a sharp transition in conductivity profiles at the boundary of matrix and fiber, while at other regions there is a gradual transition at the boundary, as shown by arrows in the image. Thus, this technique can also be used to characterize the interphase between the fiber and matrix based on the conductivity variations.

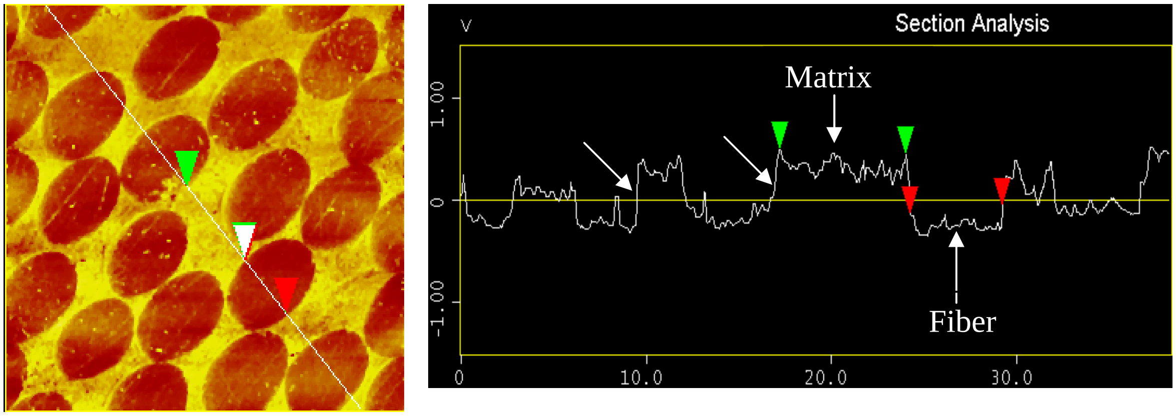

Figure 4 A section analysis of the eddy current image of fig.2. The matrix region and fiber region are indicated on the image on the right.

After characterizing the composite sample, the technique was used to characterize the carbon nanofibers of the nanocomposite sample utilizing the contrast difference between the fibers and matrix based on the conductivity. Figure 5 shows the AFM topography and eddy current image obtained on the nanocomposite sample.

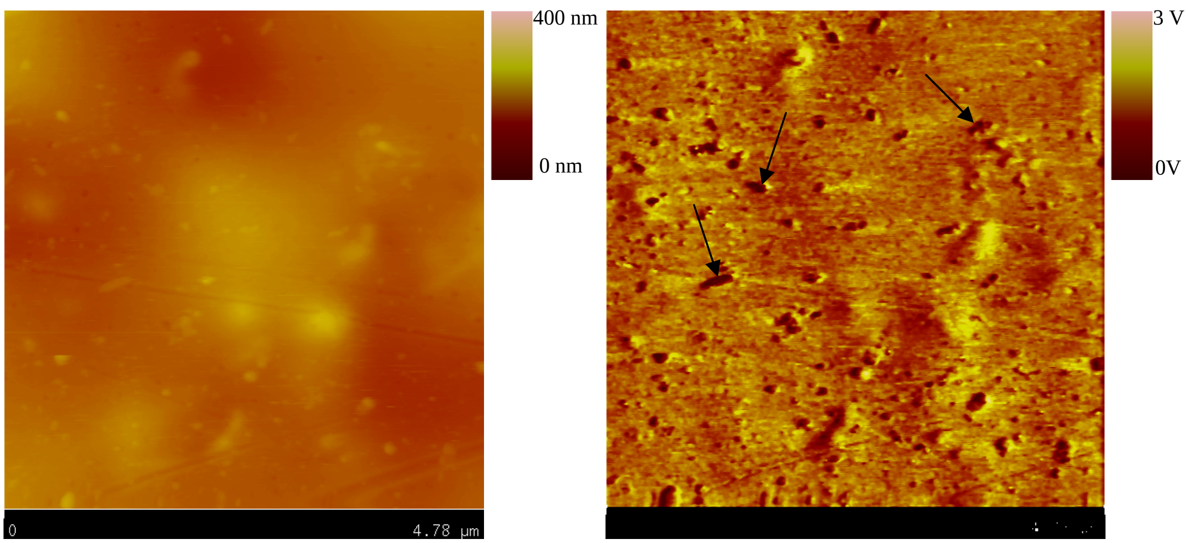

Figure 5 AFM topography (left) and eddy current (right) images of a nanocomposite thin film. Scan size 4.78 µm X 4.78 µm. Arrows on the eddy current image indicate nanofibers.

The topography of the nanocomposite film shows small hazy features in the AFM images. Even though nanofibers are present in this image, it is difficult to clearly distinguish the fibers from the matrix features. On the other hand, the eddy current image obtained in the same region shows a set of features with darker contrast. Based on the contrast obtained on the previous carbon fiber reinforced composite sample, we feel that the darker features are the carbon nanofibers in the polymer matrix. Some of the carbon nanofibers are shown by arrows in the eddy current image of fig.4. The brighter regions are the lower conductivity polymer matrix. The size of the nanofibers in this region range from 30 nm to 150 nm. The eddy current image can also be used

to quantitatively analyze the distribution and dispersion of the nanofibers in the matrix. The area fraction of the carbon nanofibers in this image (4.78 µmX 4.78 µm) is found to be approximately 8.2 %.

Figure 5 shows the topography and eddy current image obtained at another region of the nanocomposite sample. The image was taken with a scan size of 1.97 µm X 1.97 µm. Carbon nanofibers can be seen in the eddy current image with reduced contrast compared to the nonconductive polymer matrix. The size of the nanofibers in this region range from 30 nm to 150 nm.

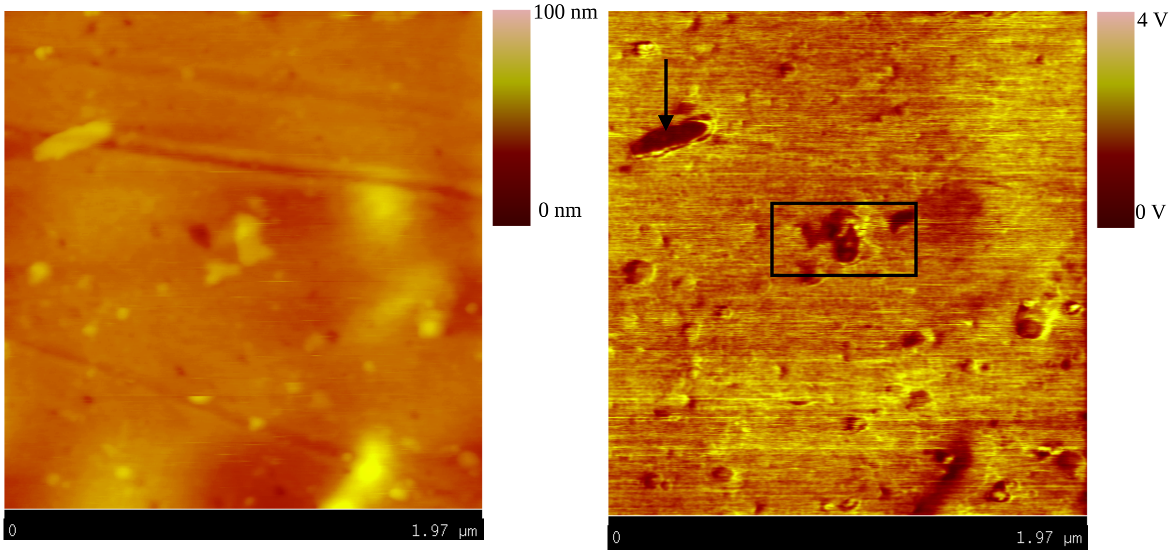

Figure 6 Topography (left) and eddy current (right) images obtained at another region of nanocomposite thin film. The arrow indicates the fiber pull-out from the matrix. Scan size 1.97 µm X 1.97 µm.

On closer observation of the eddy current image, agglomeration of the nanofibers can be observed in the image shown by the rectangular region, while the same cannot be clearly seen in the topography image. Another interesting feature of this image is indicated by an arrow in the eddy current image. The bottom region around the fiber is brighter than the top region, indicating that there is less conductivity around the bottom region than the top region. It is well known in standard eddy current testing that presence of debonding, delaminations or crack would alter the conductivity around the defects (16-19). Thus, this change in the contrast would imply a fiber pull out from the matrix. A magnified image of the debonded fiber is shown in Fig.6. A conductivity profile along the debonded fiber is shown on the right side of Fig.6.. It can be seen from this analysis that the conductivity changes sharply around the fiber where there is a pullout from the matrix. If the fiber is not pulled out from the matrix there would be a gradual transition in the conductivity profile instead of a sharp transition.

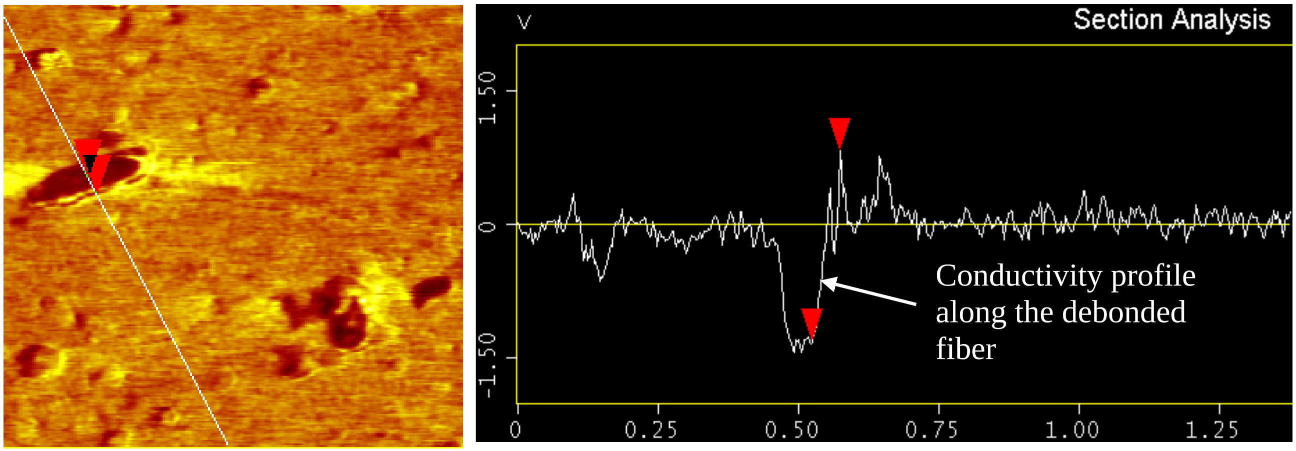

Figure 7 Conductivity profile along the debonded fiber in the nanocomposite.

4. CONCLUSIONS

An eddy current imaging technique based on Atomic Force Microscopy has been developed and used to characterize fiber reinforced polymer composites. Eddy current images have much higher contrast compared to surface topography AFM images. The contrast in the images is related to the local electrical conductivity variation in the material. In eddy current images the carbon fibers as well as carbon nanofibers are observed as dark [high conductivity] regions while the polymer matrix as bright [low conductivity] regions. Analysis of images obtained with combined AFM and eddy current techniques show that the techniques can be used to study the dispersion and distribution of the fibers in the matrix as well as fiber-matrix interface with a resolution of a few nanometers. High magnification eddy current images show non-uniform contrast around carbon fibers indicating irregularities at the fiber matrix interface. On nanofiber composites, the eddy current imaging reveals non-uniform sizes of the nanofibers and the non uniform distribution of the nano-fibers in the matrix. High resolution and high magnification eddy current images show separation of carbon nano-fibers from the polymer matrix in some regions.

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